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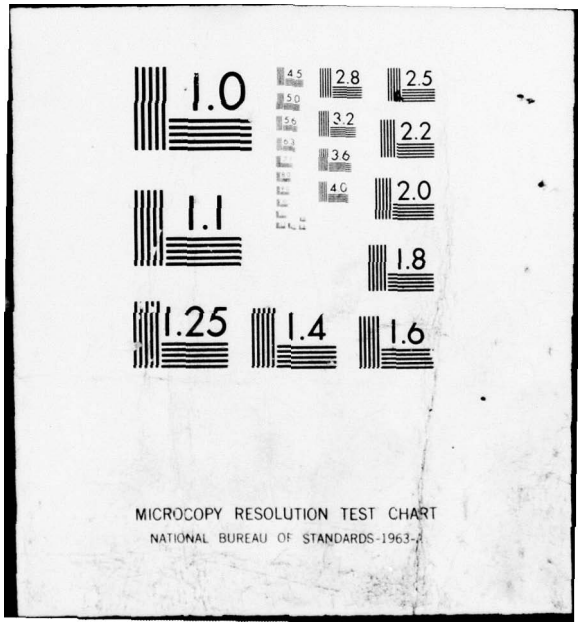
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A MODIFIED LEPS SURFACE FOR THE GROUND STATE OF THE WATER MOLECULE

Arthur Gauss, Jr.

July 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
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A Modified LEPS potential surface using a Sato parameter which is a function of the internuclear coordinates has been developed for the ground state of the water molecule. By adjusting the Sato parameter many of the known properties of the water potential are fitted with this surface.

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I. INTRODUCTION

In the Born-Oppenheimer approximation for molecular collision problems the electronic potential energy serves as the potential energy for motion of the molecular nuclei. To facilitate dynamics calculations for these problems an analytical potential surface is a very valuable tool. An analytical surface provides the necessary derivatives of the potential with respect to the internuclear coordinates over all space. An analytical surface must also be flexible enough to provide a reasonable fit to the known properties of the potential surface derived from experiment or ab-initio calculations. Many molecules or molecular complexes are characterized by having their minimum electronic potential energy in a bent configuration ($\theta \neq 0$, 180°; see Figure 1). Such molecules, of which water is an example, cannot be modeled using a standard LEPS (London, Eyring, Polanyi, Sato) surface. In this paper a modified LEPS surface is presented which can model the bent configured water molecule. While not as accurate as some other analytical methods[1,2] the modified LEPS surface is easier to apply to dynamics calculations. Modified LEPS surfaces have been developed for other systems, HO_2 and CO_2, in addition to water. Dynamics calculations are already complete for the HO_2 system.

II. MODIFIED LEPS SURFACE FOR WATER

An LEPS surface which approximates the equilibrium ground state for water (X^1A_1) has been developed. A single Sato parameter which is a function of the internuclear coordinates is used to alter the LEPS so that the water molecule in and near the equilibrium configuration can be modeled. An earlier study[3] suggested the use of large values of the Sato parameter to produce wells or barriers along the reaction path.[4] The general form of the LEPS potential is

$$V = Q_1' + Q_2' + Q_3' - [\alpha_1'^2 + \alpha_2'^2 + \alpha_3'^2 - \alpha'_1\alpha'_2 - \alpha'_1\alpha'_3 - \alpha'_2\alpha'_3]^{\frac{1}{2}} + D_2^e ,$$

1. *K.S. Sorbie and J.N. Murrell, Molecular Physics 29 (1975), 1387.*
2. *S. Farantos, E.C. Leisegang, J.N. Murrell and K. Sorbie, Molecular Physics 34 (1977) 947.*
3. *A. Gauss Jr., J. Chem. Phys 65 (1976) 4365.*
4. *J.T. Muckerman, J. Chem. Phys. 56 (1972) 2997.*

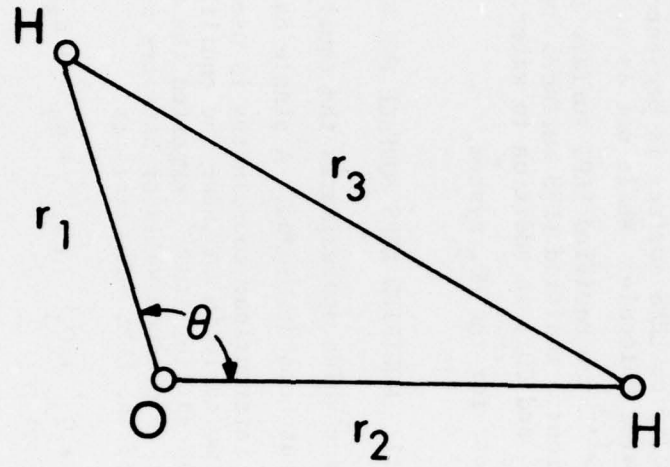

Figure 1. The internuclear distances ($r_1 r_2 r_3$) and the angle θ are defined as shown.

where

$$Q_i' = Q_i/(1+\Delta) = D_i^e/4(1+\Delta)$$
$$\times \left\{ (3+\Delta) \exp -2\beta_i(r_i - r_{i0}) - (2+6\Delta) \exp -\beta_i(r_i - r_{i0}) \right\}$$

and

$$\alpha_i' = \alpha_i/(1+\Delta) = D_i^e/4(1+\Delta)$$
$$\times \left\{ (1+3\Delta) \exp -2\beta_i(r_i - r_{i0}) - (6+2\Delta) \exp -\beta_i(r_i - r_{i0}) \right\}, \quad i = 1,2,3.$$

The Morse parameters (D_i^e, β_i, r_{i0}) are displayed in Table 1. The Sato parameter is given by

$$\Delta = A \{f(\theta)\} \{ (\sin 2\,Th)^m \}$$
$$\times \left\{ (0.94 r_1 r_2 / r^2_{10})^B \exp \left(-0.94 (r_1 r_2 / r^2_{10}) B \right) \right\},$$

where Th = Arctan (r_1/r_2) and the parameters A,m, and B are adjustable.

Table 1.

O-H	H-H
$D_1^e = D_2^e = 106.53$ kcal/mole	$D_3^e = 109.5$ kcal/mole
$\beta_1 = \beta_2 = 2.29$ Å^{-1}	$\beta_3 = 1.942$ Å^{-1}
$r_{10} = r_{20} = 0.9706$ Å	$r_{30} = 0.7417$ Å

This form of the Sato parameter could be applied to other three-atom complexes where two of the atoms are identical. It has the proper symmetry; that is, it is invariant to interchange of r_1 and r_2. A single Sato parameter has been employed here. Single Sato parameters have been used successfully by other workers on three-atom

systems where two of the atoms are identical[4,5]. The Sato parameter ranges from near zero for $r_1 = r_{10}$, $r_2 \to \infty$ (or $r_2 = r_{20}$, $r_1 \to \infty$) to slightly greater than two near the minimum energy configuration ($r_1 = r_2 \approx 0.87$ Å, $\theta = 106°$).

The function $f(\theta)$ contains additional adjustable parameters. In the case of the water molecule $f(\theta) = [\sin(Th1)]^6 + \frac{3}{4}[\sin(Th2)]^4$, where $Th1 = \frac{6}{7}\theta$ and $Th2 = \frac{1}{2}\theta$. The exponents, the constant multiplying the $[\sin(Th2)]^4$ term, and the constants multiplying θ in Th1 and Th2 are the adjustable parameters. These parameters were varied so that the potential minimum was at $\theta = 106°$, close to the actual angle of 104-105°[6]. In addition $f(\theta)$ was adjusted so that the difference between the depth of the potential well in the linear configuration and the depth in the 106° configuration was ≈ 1.8 eV (compare figs. 2 and 3), close to the 1.5 eV difference shown in the potential plot by Herzberg [7].

The second bracketed term in Δ, $(\sin 2Th)^m$, prevents the potential well from extending to large values of r_1 and r_2 along the entrance or exit valleys; it also helps eliminate the double minima near the center of the potential well (a problem when large (> 1) values of the Sato parameter are employed). A large value of the exponent, m = 16, was needed for the water potential surface.

The third bracketed term in Δ eliminates the large negative values of the potential that occur for small values of r_1 and r_2 when Δ is large. This term approaches zero as r_1 and r_2 approach zero causing the Sato parameter to approach zero and the potential (V) to form a high wall (see Figures 2,3 and 4). It goes to zero for large values r_1 and r_2 due to the exponential. By adjusting B one can ensure that the potential minimum will be near $r_1 = r_2 \approx r_{10}$. For the water molecule B=4 was chosen. For this H_2O surface the minimum is near $r_1 = r_2 \approx 0.87$ Å at $\theta = 106°$; the actual surface has its minimum at $r_1 = r_2 \approx 0.96$ Å (at θ = 104-105°)[6].

The parameter A multiplying the whole expression is chosen to insure that the depth of the potential well (at $\theta \approx 106°$) is close to the experimental value. In the case of the water molecule $A = 10^2$ was chosen. This value makes the well depth ≈ 5 eV below the zero of

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5. *M. Baer, J. Chem. Phys. 60 (1974) 1057.*
6. *B.J. Rosenberg, W.C. Ermler and I. Shavitt, J. Chem. Phys. 65 (1976) 4022.*
7. *G. Herzberg, Electronic spectra of polyatomic molecules (Van Nostrand, Princeton, 1966).*

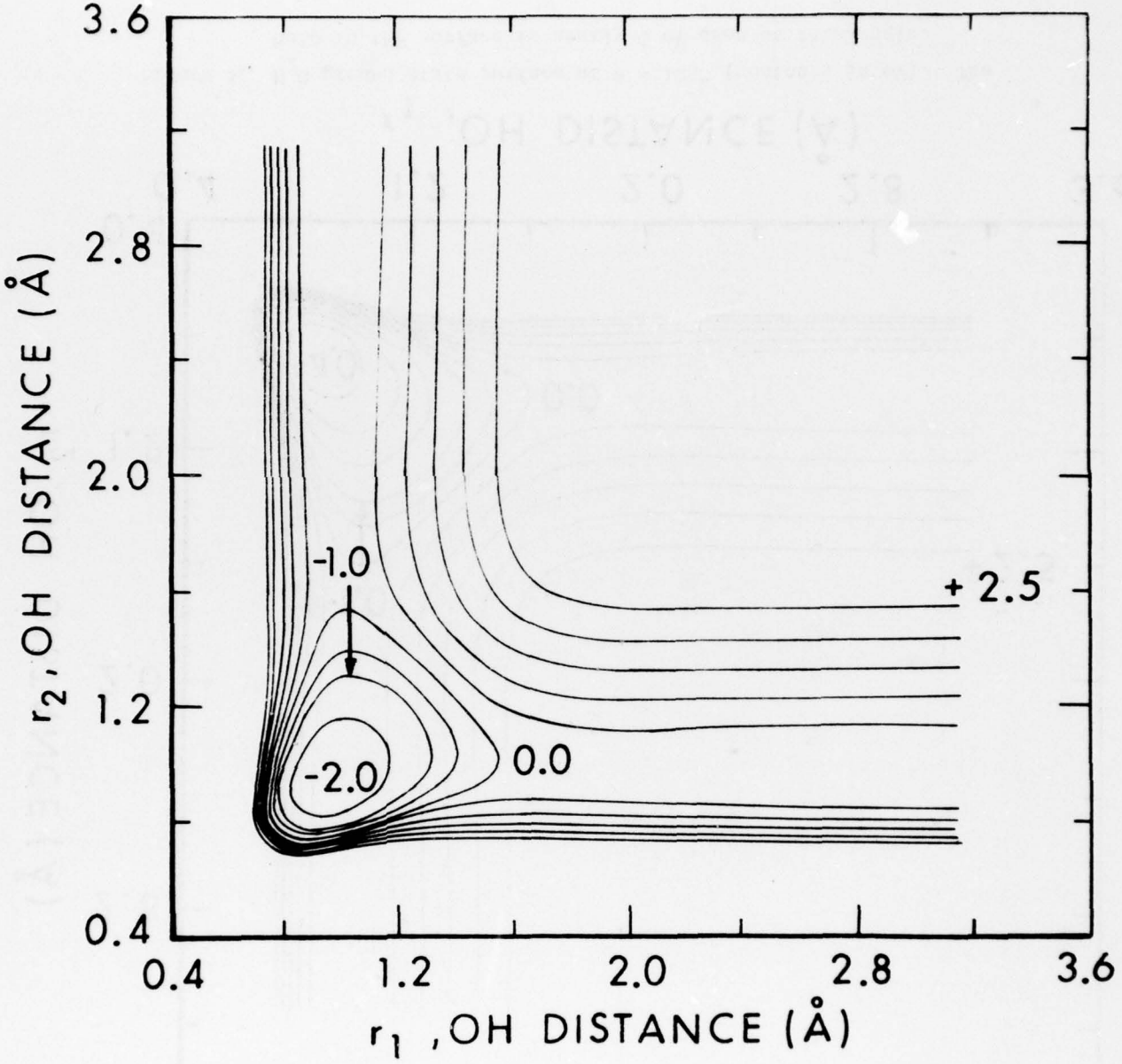

Figure 2. H_2O ground state surface for $\theta = 170°$ (contours in eV).

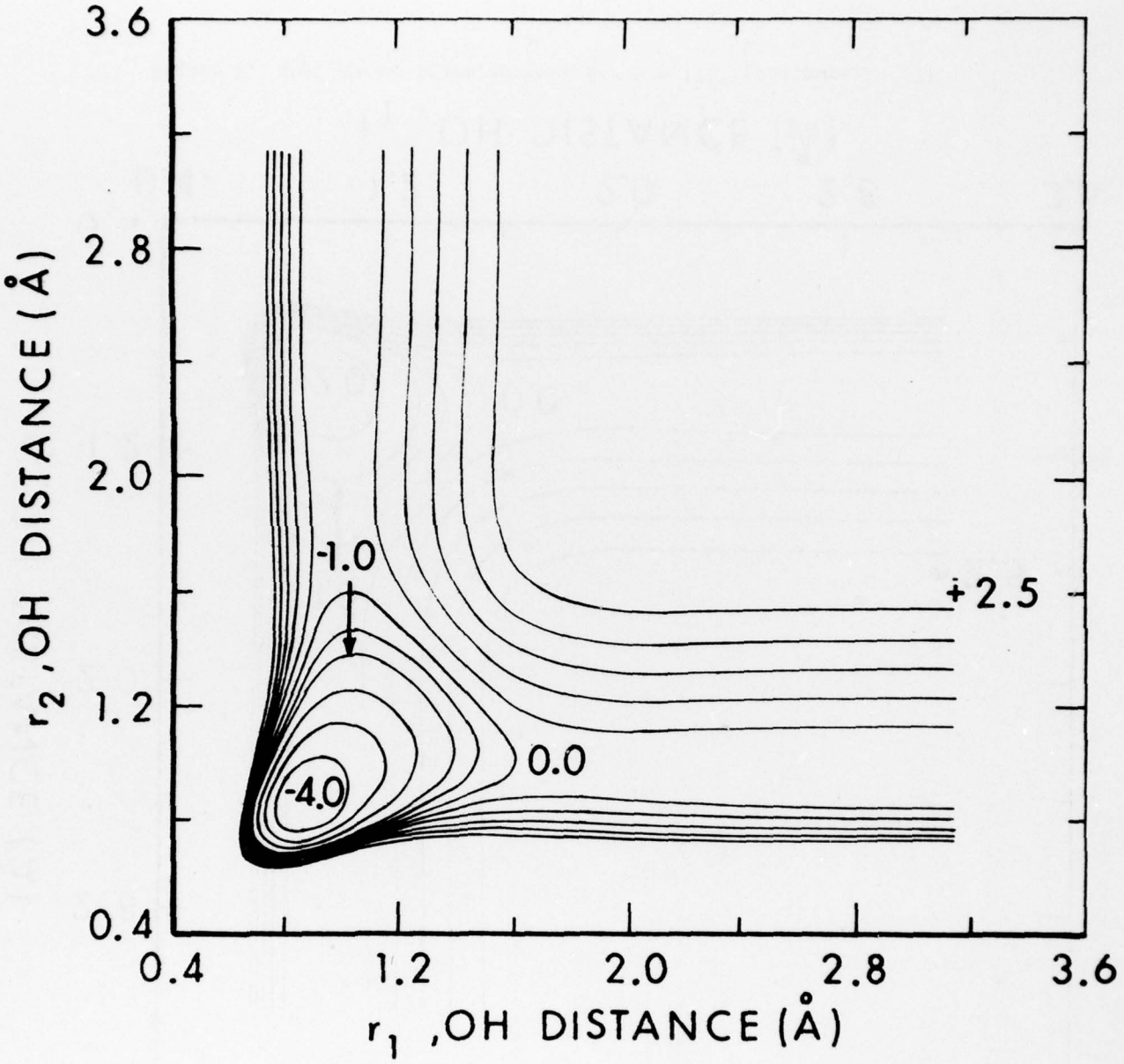

Figure 3. H_2O ground state surface at $\theta = 105°$ (contours in eV). The hole in the surface is nearly 5 eV deep at this angle.

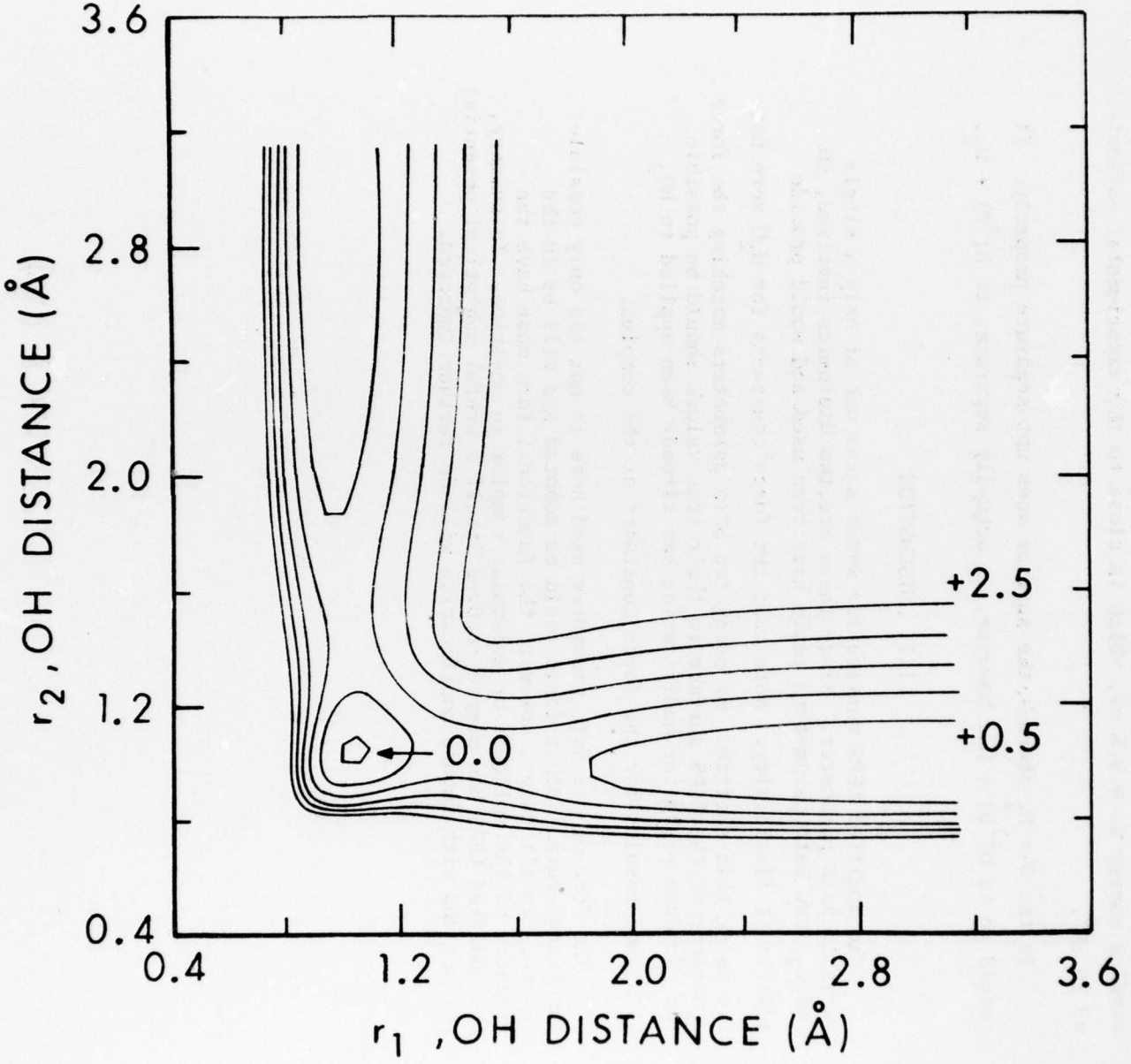

Figure 4. H_2O ground state surface for $\theta = 60°$ (contours in eV).

the potential, the separated OH ($^2\Pi$) + H (^2S) state. Thus the overall binding energy is ≈ 9.5 eV, which is close to the experimental estimate of 10 eV[8].

In the O + H_2 channel the surface does not separate properly. It should go to $O(^1D)$ + H_2; however, it actually separates to $O(^3P)$ + H_2.

III. DISCUSSION

The modified LEPS surface for water makes use of only a single variable Sato parameter. Since there are two diatomics involved, OH and O_2, two Sato parameters could have been used and would provide additional flexibility. Note that the force constants for H_2O were not fit using this surface. By using two Sato parameters matching the force constants of the LEPS surface to their true values should be possible. The two Sato parameter modification has already been applied to HO_2 with good results for the force constants of the complex.

The form of the Sato parameter used here is not the only possible functional form. Other forms could be adopted and will be in the future. In all cases, however, the functional form must have the symmetry of the molecule or molecular complex in question. In summary, the modified LEPS has already proved itself a useful analytical potential surface and with future modification will be further improved.

8. *B.J. Rosenberg and I. Shavitt, J. Chem. Phys. 63 (1975) 2162.*

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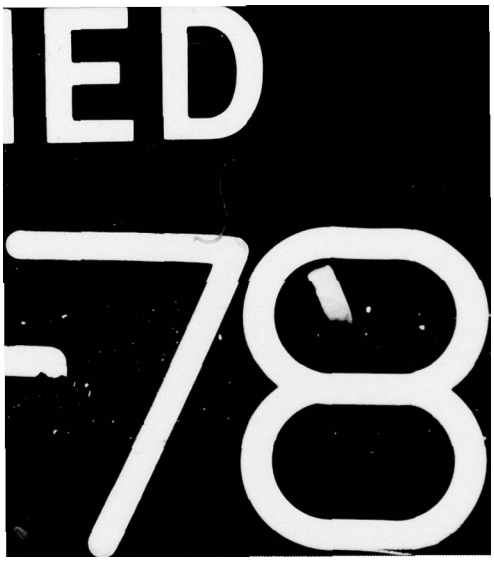
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